

SCIENCE FOR CERAMIC PRODUCTION

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PIGMENTATION OF CLAYS OF THE GZHEL' DEPOSIT

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Using the Mössbauer spectroscopy method, the authors established variations in the color of clay minerals depending on the main chromophore, namely, iron, its valence, coordination number, and closest environment, and the distortion of the coordination polyhedron. The color of the Gzhel' deposit clays depends on the presence of differently colored phases and their quantitative content.

There are as many natural clay varieties as there are clay deposits. This is due to the different conditions of clay formation. Clay beds formed by sedimentation rarely have a homogeneous composition. In most cases the beds have a stratified or laminar structure, and each seam or stratum contains a special clay variety that has its own color, density, content of mineral and organic impurities, and thickness. Any clay deposit and each seam have their own geological history [1].

According to a geological survey carried out in 1986–1987 by the Moscow Geological Survey Expedition, the variegated clays of the Gzhel' deposit belong to upper carboniferous deposits. Clay from the Gzhel'-Kudinovskoe suite is of maritime genesis.

There is a certain regularity in the color of the clay bedding in the Gzhel' tier. Green-colored or variegated dense plastic clays are located above a lime stratum at a depth of 7–23 m, and dark brown and grayish brown clays are situated over the green and variegated clays. Red clays occur above the dark brown and grayish brown clays, and inside the red-clay layer there is an alternation of red and gray or grayish-blue clays. Loam is bedded above the red clays, and a soil-and-vegetal layer not more than 0.5 m thick is found above the loam.

The layout of the clays may vary depending on the geographic position of the Gzhel' deposit site. Site No. 3 (Fig. 1), which is located 1 km north of the western boundary of Rechitsa village, is formed by two colored layers: a variegated and a red one, whereas site No. 1, located 1 km northeast of Konyashino village, is characterized by a more complex clay bedding, although the position of the green and red clays at both sites is the same. In contrast to site No. 3, site No. 1 contains additional clay varieties: light blue, gray, gray-blue, and grayish-green.

An analysis of over 110 clay samples obtained in the course of the geological survey in the Gzhel' deposit showed that the ceramic properties of the clay can be predicted from its color. Thus, green, grayish-green, gray, light gray, dark gray, and light blue clays have a denser structure, higher plasticity, finer dispersion (the content of the fraction below 1 μm reaches 42.4%), increased fire shrinkage (4.4% at a temperature of 1000°C), and decreased porosity after firing at 1000°C (7–10.7%) as opposed to red, variegated, and red-brown clays.

For the purpose of studying the origin of clay coloring in the Gzhel' deposit, the effect of impurities, the mineral and chemical composition, and other clay characteristics on its color was investigated.

It is known that clays usually occur under a layer of humus and brown or bituminous coal and experience the action of carbonic acid and humus material profusely released by

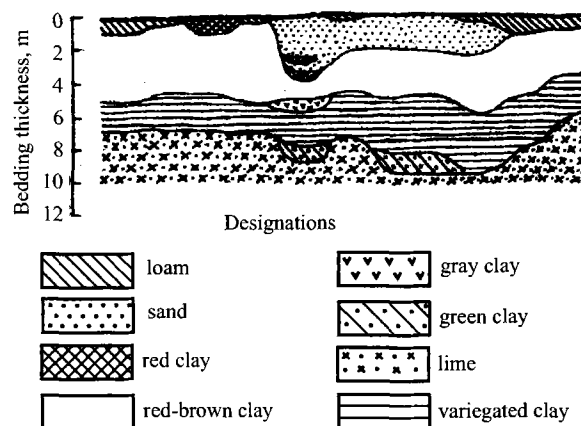


Fig. 1. Schematic cross section of site No. 3 of the Gzhel' deposit of low-melting clays.

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TABLE 1

Clay	Sample*	Weight content, %												
		SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	calcina- tion loss	CO ₂	organic impu- rities	SiO ₂ non-free
Red-brown	202/1	66.30	14.45	0.60	6.43	2.68	1.22	0.29	4.01	0.06	4.70	0.93	0.25	32.10
Light brown	4/2	61.98	16.67	0.85	5.00	3.43	1.24	0.23	5.62	Traces	5.47	2.15	0.41	28.75
Dirty red	204/1	59.68	16.87	0.81	7.66	2.23	1.57	0.20	6.52	The same	4.47	0.44	0.42	28.30
Red-grayish brown	206/1	58.90	16.50	0.81	7.83	2.73	1.75	0.24	6.40	0.05	4.70	0.66	0.29	25.85
Bright brown	2/5	57.22	17.13	0.81	7.18	3.17	1.91	0.21	5.84	0.04	6.03	1.93	0.55	25.0
Red-brown	10/3	56.94	17.41	0.85	6.24	4.22	1.91	0.21	5.97	0.06	6.65	2.58	0.14	28.00
Red	8/3	57.76	15.74	0.80	6.57	4.03	1.90	0.23	5.84	0.05	6.68	2.20	0.12	25.30
Red-grayish brown	205/1	57.88	16.67	0.78	8.00	2.98	1.92	0.20	6.24	0.07	5.08	1.10	0.44	26.40
Bright red	11/2	59.14	16.02	0.74	6.57	2.89	1.98	0.23	6.40	0.14	5.32	1.48	0.15	25.00
Gray-brown	10/4	59.20	17.26	0.78	7.44	1.75	2.05	0.23	6.40	0.01	4.82	0.55	0.20	25.55
Gray-reddish	201/1	58.00	16.80	0.81	8.18	2.48	2.10	0.24	6.10	Traces	5.31	0.65	0.29	26.95
Gray	201/2	59.14	17.91	0.70	6.43	2.19	2.10	0.23	6.40	0.04	4.68	0.44	0.24	22.25
Gray	4/4	60.16	17.33	0.74	6.57	1.66	2.20	0.26	6.24	0.02	4.79	0.22	0.24	28.25
Dark beige	11/3	57.30	15.58	0.78	6.42	4.65	2.27	0.26	5.84	0.07	7.04	2.64	0.09	23.30
Dirty red	203/1	57.50	17.10	0.81	8.53	1.98	2.45	0.20	6.72	Traces	4.95	0.44	0.29	24.00
Dark red-brown	11/1	58.72	16.06	0.82	6.86	2.37	2.49	0.23	6.24	0.15	5.45	1.48	0.20	26.10
Light gray	10/5	56.98	16.20	0.67	5.98	3.20	2.78	0.21	6.24	0.28	6.88	2.09	0.20	29.25

* All samples acquire a red color after firing in an oxidizing medium.

these organic strata. The role of humus acid and carbonaceous substances released from it as a consequence of carbonization involves their ability to absorb air oxygen from the ambient medium and reduce oxide compounds. Thus, these agents can reduce trivalent iron to bivalent iron, which forms a soluble compound in water [1].

Ferric oxide is the principal chromophore in clay, and as its content increases, the intensity of the red color can increase as well. At the same time, organic impurities impart dark gray colors to clay, and carbonaceous substances (humus, lignite) with their content ranging from 0.5 to 20% impart black and brown colors [1].

According to Avidon [2], the difference in the coloring of clays is sometimes caused by a difference in their chemical composition. In some areas of a deposit carbonaceous material imparts a black color to the clay, whereas at some distance from those places the same stratum can be white or light gray due to a lower content of carbonaceous impurities.

The chemical compositions of the clays discovered in the Gzhel' deposit (Table 1) are rather similar, in spite of their color differences.

Thus, organic impurities are present in gray (samples 10/4, 201/1, 201/2, 4/4, 10/5) and red (samples 202/1, 206/1, 11/1, 203/1) clays in virtually equal quantities: 0.20 – 0.29%. The ferric oxide content can be equal in gray (samples 202/2, 4/4) and red (samples 8/3, 10/3) clays.

The effect of magnesium oxide on the variations in the clay color should be noted. With an insignificant increase in the magnesium oxide content, the color of the clay can change from red through gray to light gray. The transition from red to gray color was observed at a magnesium oxide content over 2%. However, an exception was found in red-colored clays (Table 1, samples 203/1 and 11/1) in which the content of magnesium oxide is higher than in gray clays.

Clay coloring is caused by the presence of soluble iron compounds. An additive of tannic acid produces an extremely variegated pigmentation in clays, which is due not to different degrees of dispersion of iron but to a varying concentration of H⁺ or (OH)⁻ ions. The intensity of the coloring depends on the amount of dissolved iron [1].

As a result of determining the content of (OH)⁻ ions in differently colored Gzhel' deposit clays, it was established (Table 2) that although the aqueous clay extracts have virtually equal (OH)⁻ ion content (0.80 – 0.82 mg-eq), their coloring is different (gray, lilac), which contradicts Zalmang's assertions.

Since chemical analysis does not give the reason coloring for the of Gzhel' argillaceous rocks, x-ray and Mössbauer analyses of these

TABLE 2

Sample	Ion content in aqueous extract, mg-eq per 100 g of material						
	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	(OH) ⁻	Cl ⁻	(SO ₄) ₂ ⁻
Gzhel' clay, sample 1 (gray):							
water-soluble salts, pH = 8.4	0.9	0.16	0.11	0.08	0.80	0.26	0.30
absorbed bases	17.60	3.60	0.32	0.35	—	—	—
Gzhel' clay, sample 2 (lilac):							
water-soluble salts, pH = 8.5	0.60	0.20	0.14	0.12	0.82	0.22	0.15
absorbed bases	20.80	4.96	0.33	0.37	—	—	—

TABLE 3

Clay type and impurities	Clay color													
	pink	white	light gray	gray	yellowish white	green	light blue	greenish-light blue	variegated	red	violet	grayish brown	dark brown	black
Kaolinite	—	+	+	—	+	—	—	—	—	—	—	—	—	—
Hydromusovite	—	+	+	—	+	—	—	—	—	—	—	—	—	—
Monothermite	—	+	+	—	+	—	—	—	—	—	—	—	—	—
Montmorillonite	—	+	+	+	+	+	+	+	—	+	+	—	—	—
Hydromica	—	—	—	—	—	+	+	—	+	—	—	—	—	—
Beidellite	—	—	—	+	—	+	+	—	—	—	—	—	—	—
Nontronite	—	—	—	—	—	+	+	—	—	—	—	—	—	—
Impurities:														
organic	—	—	+	+	—	—	—	—	—	—	—	—	—	+
in finely dispersed form:														
Fe oxides	+	—	—	—	—	—	—	—	—	+	+	—	—	—
ferric hydroxide	—	—	—	—	—	—	—	+	—	—	—	—	—	—
manganese oxide	—	—	—	—	—	—	—	—	—	—	—	+	—	—
chlorites	—	—	—	—	—	+	+	—	—	—	—	—	—	—
glauconites	—	—	—	—	—	+	+	—	—	—	—	—	—	—
nickel compounds	—	—	—	—	—	+	+	—	—	—	—	—	—	—

clays were performed with the purpose of determining the effect of the mineral composition, the form of incorporation of iron, the impurities, etc. on the color of the clay.

It is known that single-mineral clays usually have light gray, white, and sometimes light greenish and bluish colors. Some hydromica (including glauconite), montmorillonite, and nontronite clays have a white color and various shades of red, green, and light blue pigmentation. The pigmentation of montmorillonite clays varies but the most typical is white, light gray, pale yellowish-green, gray, and greenish-sky-blue; less frequently red and purple colors of various shades are found. Impurities of different compounds even in small quantities cause changes in the color of clay rocks. Oxides and hydroxides, especially in a finely dispersed form, impart to clays different shades of yellow, pink, red, and purple colors, and manganese oxides makes clays brown. Bitumen imparts light and darker brown shades to clays. Impurities of chlorites, glauconites, and nickel compounds cause the appearance of greenish and light blue shades of various brightness and intensity [2].

Table 3 lists the coloring of different types of low-melting clays used in ceramic production for building ceramics, majolica, pottery, etc.

Variegated clays of the Gzhel' deposit (red, gray, green, multicolored, black, gray-green, brown, lilac) were subjected to x-ray analysis on an ADP-1 diffractometer.

The identification thresholds in the studied samples were as follows (%): quartz 0.5, goethite 3, montmorillonite 5, illite 1–2, hematite 1–3, feldspar 1, chlorite 1, siderite 1, pyroxene 1, pyrite 1.

The x-ray analysis revealed the presence of a number of minerals in the clays: quartz, hydromica, kaolinite, feldspar, calcite, montmorillonite, siderite, dolomite, chlorite, hematite, goethite. The following minerals occupy the leading place by their quantitative content: montmorillonite over

45%, hydromica 10–20%, kaolinite 1–5%, chlorite up to 2%, and pyroxene up to 3%.

The crystalline phase of the sand-aleurite fraction is mostly comprised of: quartz up to 20%, calcite 1–5%, feldspars up to 9%, and siderite and dolomite 1–5%.

In clay with a low content of hematite and goethite, a reddish-brown color was registered and it was found that small goethite veins do not participate in color modification. A greenish shade is imparted to clays by illite (over 10–12%) in the absence of hematite and by goethite in small quantities (traces). The greenish shade in clays can become more intense in the presence of chlorite. In the case of the simultaneous presence of greenish illite and red-brown ferric hydroxide, the clay had a lilac color.

Iron is one of the most common color centers in many minerals, and therefore, pigmentation of minerals caused by this chromophoric element can be studied using the Mössbauer spectroscopy method on Fe⁵⁷. This method can supply comprehensive and reliable information on the form of incorporation of iron in the mineral, its valence, the number of structural positions occupied, the extent of their filling, and the distribution. It is possible to assess the redox processes in mineral formation based on the ratio of bivalent and trivalent iron.

Mössbauer measurements (Fig. 2) of clays with different colors were carried out on a YaGRS-4M spectrometer with a γ -radiation Co⁵⁷ source in a rhodium matrix. For the analysis samples weighing 0.2 g milled to a particle size of 0.05–0.07 mm were used. The NGR (nuclear gamma resonance) spectrometer functioned in a mode of constant acceleration with an AI-256 pulse analyzer. The measurements were carried out at room temperature. The calibration of the experimental NGR spectra was carried out based on α -Fe₂O₃ peaks with their known positions on the velocity scale. The NGR spectra were processed graphically using the Lorentz

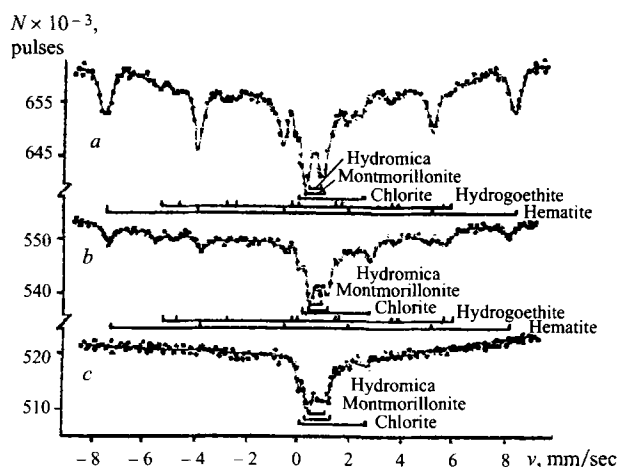


Fig. 2. Mössbauer spectra of Gzhel' deposit clay samples: a) variegated, b) lilac, c) grayish-green.

description of resonance lines. In doing so, the peaks in Fe^{3+} doublets were taken to be equal, and the asymmetry of the

resonance lines was taken into account in Fe^{2+} doublets of laminar silicates. The threshold of identification of iron using Mössbauer spectroscopy was 0.5%.

Results of the Mössbauer analysis are shown in Table 4. The diagnostics of paramagnetic iron-containing phases was carried out based on the isomeric shift and the quadrupole splitting, and magnetically ordered phases were studied based additionally on the effective fields on the Fe^{57} nuclei. It should be noted that the hematite in the Gzhel' deposit clays differs from standard hypogenic hematite (515 kOe) by decreased values of the magnetic fields on the Fe^{57} nuclei (479 – 507 kOe). This can be explained by a high dispersion of the particles [3] or isomorphic incorporation of Al^{3+} in the lattice [4]. The presence of two sextuplets in the NGR spectra of $\alpha\text{-FeOOH}$ indicates that the hydroxide is hydrogoethite, and the fluctuations of their magnetic fields can be explained by a different content of water (higher than in the monohydrate). Finely disperse hydroxides can be manifested in the form of doublets [5]. According to their Mössbauer parameters, finely disperse hydroxides are close to hydromica,

TABLE 4

Sample*	Characteristics of Gzhel' deposit clay samples	Fe component minerals	Isomeric shift, mm/sec	Quadrupole splitting, mm/sec	Effective magnetic field, kOe	Fe oxidation coefficient (total)	Iron distribution among phases, rel.%/wt.%
1	Variegated	Hematite (Fe^{3+})	0.65	0.3	479		37.5/2.21
		Hydrogoethite (Fe^{3+})		Not determined			16.7/0.98
		Finely disperse hydroxides and hydromica (Fe^{3+})	0.60	0.40	0	0.9	18.7/1.10
		Montmorillonite (Fe^{3+})	0.60	0.65	0		16.7/0.98
		Chlorite, mica (Fe^{2+})	1.40	2.5	0		10.4/0.61
2	Gray from variegated	Montmorillonite (Fe^{3+})	0.60	0.70	0		36.0/1.24
		Finely disperse hydroxides and hydromica (Fe^{3+})	0.50	0.50	0	0.72	36.0/1.24
		Chlorite, mica (Fe^{2+})	1.40	2.70	0		28.0/0.96
3	Red from variegated	Hematite (Fe^{3+})	0.46	0.33	507		30.3/1.72
		Montmorillonite (Fe^{3+})	0.50	0.70	0		35.8/2.04
		Chlorite, mica (Fe^{2+})	1.20	2.50	0	0.92	7.5/0.43
		Finely disperse hydroxides and hydromica (Fe^{3+})	0.50	0.50	0		11.3/0.64
		Hydrogoethite (Fe^{3+})		Not determined			15.1/0.86
4	Green	Montmorillonite (Fe^{3+}) (Ca)	0.60	0.70	0		51.9/2.08
		Hydromica (Fe^{3+})	0.50	0.45	0		14.8/0.59
		Chlorite, mica (Fe^{2+})	1.35	2.70	0	0.78	22.2/0.89
		Hydrogoethite (Fe^{3+})		Not determined			11.1/0.45
		Hematite (Fe^{3+})	0.25	0.70	451		16.7/0.94
5	Lilac	Montmorillonite (Fe^{3+})	0.60	0.70	0		33.3/1.88
		Hydrogoethite (Fe^{3+})		Not determined			18.0/1.01
		Finely disperse hydroxides and hydromica (Fe^{3+})	0.50	0.45	0	0.85	17.4/0.98
		Chlorite, mica (Fe^{2+})	1.40	2.70	0		14.6/0.98
		Montmorillonite (Fe^{3+}) (Ca)	0.6	0.75	0		76.9/2.89
6	Gray	Hydromica (Fe^{3+})	0.6	0.45	0	0.88	11.0/0.41
		Chlorite, mica (Fe^{2+})	1.5	2.7	0		12.1/0.45
		Hematite (Fe^{3+})	0.54	0.18	499		49.6/3.16
		Montmorillonite (Fe^{3+})	0.50	0.60	0		24.8/1.58
		Finely disperse hydroxides and hydromica (Fe^{3+})	0.55	0.50	0	0.89	8.3/0.53
7	Dark brown	Hydrogoethite (Fe^{3+})		Not determined			6.6/0.42
		Chlorite, mica (Fe^{2+})	1.25	2.55	0		10.7/0.68

* Error of determination of the isomeric shift ± 0.02 mm/sec, quadrupole splitting ± 0.02 mm/sec, effective magnetic field ± 5 kOe, phase content 10%.

and therefore, Table 4 presents the total relative content of iron associated with these phases.

The montmorillonites proved different according to their Mössbauer parameters. This is especially noticeable in the values of the quadrupole splitting. A comparison of the data on quadrupole splitting as the most structurally sensitive parameter with the data on interplanar distances in montmorillonite (Fig. 3) revealed the following relationship: as the content of Ca ions in the montmorillonite increases, the interplanar distance increases as well, due to their larger ionic radius. At the same time, the local distortions of coordination polyhedra occupied by Fe^{3+} ions increase, which results in increased quadrupole splitting of these ions, since for Fe^{3+} the degree of distortion of a polyhedron is in direct relation to the quadrupole splitting. The results obtained support the existence of calcium and sodium varieties of montmorillonite in the Gzhel' clays and indicate the applicability of Mössbauer spectroscopy for these purposes.

The Mössbauer analysis of Gzhel' clays of different colors made it possible to establish the effect of hematite on the color of the clay.

The ratio of di- and trivalent iron is an important characteristic of the redox environment. It is convenient to use the iron oxidation coefficient (total) defined as $K_{\text{ox}} = \text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ as a criterion in Mössbauer spectroscopy. As follows from the data presented (see Table 4), the iron oxidation coefficient is higher in red clays than in green and gray clays. Whereas in red clays of different shades K_{ox} varies within the range of 0.89–0.93, in green and gray clays it varies from 0.73 to 0.88. These data indicate that the formation of red-colored clays took place in a more alkaline medium than that of green and gray clays.

According to data of Grum-Grzhimailo [6], the most common chromophoric elements can cause different pigmentation in minerals, depending on their valence and coordination (Table 5).

The data in Tables 4 and 5 show that whereas the color of a specific mineral depends on the type of chromophore and its valence, coordination number, and environment, the color of a rock is determined by the content of differently colored minerals in this rock. It is the proportion of these minerals that imparts different shades to rocks. Thus, a higher content of hematite (Fe^{3+} in sixfold coordination of oxygen atoms) in the samples imparts an orange or yellow color to them (samples 1, 3, 5, 7). An increase in the chlorite content in the clays (Fe^{2+} in sixfold coordination of oxygen atoms and OH groups) imparts a green color to them (sample 4), and a gray color is caused by the presence of montmorillonite, hydro-mica, and organic matter. The studies showed that the rock color changes with increasing iron content in the oxide phases. The brown color of goethite is less contrasting, and in the presence of hematite it is not a deciding factor in the rock color.

The results obtained in mixing hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite with finely pulverized kaolin from the Prosyantov-

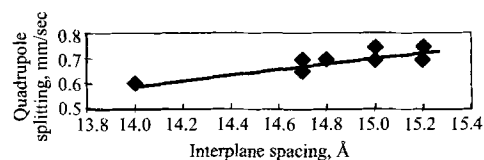


Fig. 3. Quadrupole splitting of Fe ions as a function of the interplane spacing in montmorillonite.

skoe deposit in various ratios (Table 6) attested to a change in the pigmentation from lilac to dark red in the samples with hematite and to cream, beige, and ocher in the samples of kaolin with goethite.

Thus, the color of clays from the Gzhel' deposit characterizes the rock formation environment, the mineral and chemical composition of the rock, the form of incorporation of iron, and the physicommechanical properties of the clay: plasticity, shrinkage, porosity. Therefore, by mixing clays of different colors it is possible to predict and regulate the tech-

TABLE 5

Chromophore	Coordination number	Color produced	Typical mineral
Fe^{2+}	6	Green	Olivine
	6	Light blue	Aquamarine
	8	Red	Almandine
Fe^{3+}	6	Dark brown, brown	Goethite
	6	Green	Demantoid
	4	Yellow, yellow-green	Orthoclase
$\text{Fe}^{2+} + \text{Fe}^{3+}$	6	Blue	Vivianite
	6	Black	Egirine
	6	Green	Tourmaline
Mn^{2+}	6	Pink	Rhodochrosite
Mn^{3+}	6	The same	Peidmontite

TABLE 6

Sample	Weight content, %			Color
	kaolin	hematite	goethite	
1	90	10	—	Light light lilac
2	80	20	—	Light lilac
3	70	30	—	Lilac
4	60	40	—	Cherry-lilac
5	50	50	—	Dark lilac-cherry
6	40	60	—	Lilac-cherry-brown
7	30	70	—	Cherry-brown
8	10	90	—	Dark cherry-brown
9	90	—	10	Light cream
10	80	—	20	Cream
11	70	—	30	Light beige
12	60	—	40	Beige
13	50	—	50	Dark beige
14	40	—	60	Light ocher
15	30	—	70	Ocher
16	10	—	90	Dark ocher

nological processes in ceramic production and impart desirable shades of red color to the finished ceramics.

REFERENCES

1. G. Zal'mang, *Physicochemical Foundations of Ceramics* [Russian translation], Moscow (1959).
2. V. P. Avidon, *Preliminary Testing of Clay under Field Conditions* [in Russian], Moscow (1968).
3. W. Kunding, H. Bommel, G. Constabaries, and P. H. Lindquist, "Some properties of supported small α -Fe₂O₃ particles determined with the Mössbauer effect," *Phys. Rev.*, **142**(2), 327 – 353 (1966).
4. C. Janot and H. Gibert, "Les constituants du fer dans certaines bauxites naturelles etudiées par effect Mössbauer," *Buil. Sos. Er. Miner.: Cristallogr.*, **93**(2), 213 – 223 (1970).
5. É. P. Nikolaeva, I. S. Spirina, V. V. Korovushkin, et al., "Ferrous minerals in complex oxidized ores," *Zapiski Vsemir. Mineral. Obshch.*, No. 4, 478 – 489 (1986).
6. S. V. Grum-Grzhimailo, "Coloring of mineral stones," *Zapiski Vsemir. Mineral. Obshch.*, **87**, Issue 1, 125 – 150 (1959).